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PATENT ABSTRACTS OF JAPAN

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(54) BATTERY ELECTRODE AND BATTERY

(57)Abstract:

PURPOSE: To provide a battery electrode developing superb battery characteristics by using surface modified carbon powder having a surface active agent adsorbed onto the surface in place of the carbon powder.

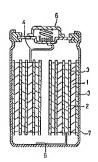
CONSTITUTION: Carbon powder is soaked in a liquid formed by dispersing surface active agent in a low boiling point solvent such as water or alcohol and the like.

point solvent such as water of alcohol and the line.

Thereafter the solvent is evaporated, and the surface active agent is effectively adsorbed to the carbon powder. Hereat, a battery BA1 is composed of a positive electrode 1, a negative electrode 2, a separator 3 for isolating both electrodes, a positive electrode lead 4, a negative electrode lead 5, a positive electrode external terminal 6 and a

negative electrode can 7. And the positive electrode 1 and negative electrode 2 are rolled up in spiral, through the separator 3 in which a nonaqueous electrolyte is poured to be contained in the negative electrode can 7. And the positive electrode 1

is connected to the external terminal 6 through the lead 4, and the negative electrode 2 is connected to the negative electrode can 7 through the lead 5, and the chemical energy generated inside the battery BA1 is brought out to the outside as the electrical energy. When the surface



modified carbon powder is applied to the electrodes, electrodes of, the battery which can develope superb battery characteristics can be obtained.

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CLAIMS

[Claim(s)]

[Claim 1]An electrode for cells, wherein the end of surface treatment carbon powder which it is an electrode for cells which makes positive electrode mixture which consists of an active material, a carbon powder end as a conducting agent, and a binder come to adhere to a charge collector, and made a surface-active agent stick to the surface as said end of carbon powder is used.

[Claim 2]The electrode for cells according to claim 1 in which said end of surface treatment carbon powder is a thing which makes said surface-active agent come to stick to 100 weight sections at a rate of less than ten weight sections in said end of carbon powder.

[Claim 3]The electrode for cells according to claim 1 in which said active material is at least a kind of metallic oxide chosen from a group which consists of LiCoO₂, LiMn₂O₄, LiMnO₂, LiMnO₂, and CuO.

[Claim 4]A cell which uses the electrode for cells according to any one of claims 1 to 3 as an anode.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]This invention relates to the wettable (Ilquid-containing capacity) improvement to the electrolysis solution of the electrode for cells in detail with respect to the electrode for cells.

[0002]

[Description of the Prior Art]As an active material of the anode of nonaqueous cells, such as a lithium cell, although the powder of metallic oxides, such as LiNiO₂ and LiCoO₂, is used, since a metallic oxide is a non-conducting substance, a conducting agent is blended that conductivity

should be given to this and it is used as positive electrode mixture.

[0003]That is, the anode of a nonaqueous cell kneads first a powdered active material and the conducting agent which consists of the end of carbon powder with binders, such as a fluoro-resin, produces positive electrode mixture, and is produced by subsequently to a charge collector (axis) sticking this positive electrode mixture by rolling or other means. since an electrode reaction occurs by the contact interface of an active material and an electrolysis solution in the case of this kind of electrode, only the portion (the following -- "-- it gets wet and part" is called) which carries out direct contact to an electrolysis solution among all the surfaces of an active material will participate in an electrode reaction. That is, the area of the portion which gets wet with the electrolysis solution turns into effective surface area of an active material.

[0004]However, wettability [generally as opposed to an electrolysis solution regardless of a drainage system and a nonaqueous electolyte] is not good the end of carbon powder. If the end of carbon powder which is not good as for this wettability is blended as a conducting agent as it is, the wettability of the active material which lives together will also become not good. It ** and only a cell with small cell capacity becomes difficult to get. If the wettability of an active material is not good, namely, in the account of the upper, the electrode reaction in an anode will get wet, and will come to occur intensively in a part, it will get wet, and the degradation speed of the active material of a part will become guick. It was a solution to the surface of an active material.

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an electrode for rechargeable batteries, only the cell which is not good as for a cycle characteristic becomes difficult to get.

[0005]This invention is made in view of the above situation, and the place made into the purpose is to provide the cell which uses for an anode the electrode for cells and it which may make the outstanding battery characteristic reveal.

[0006]

[Means for Solving the Problem]An electrode for cells concerning this invention for attaining the above-mentioned purpose, The end of surface treatment carbon powder which it is an electrode for cells which makes positive electrode mixture which consists of an active material, a carbon powder end as a conducting agent, and a binder come to adhere to a charge collector, and made a surface-active agent stick to the surface as said end of carbon powder is used.

[0007]An electrode for cells concerning this invention may be suitably used, for example as an anode of a nonaqueous electolyte lithium cell.

[0008] In this Invention, a thing to which a surface-active agent was made to stick is used as the end of conducting agent slack carbon powder.

[0009]As the end of carbon powder, carbon black, acetylene black, and the Ketzin black are illustrated. Such conductive powder may use a kind independent and may use two or more sorts together if needed.

[0010]It will not be restricted especially if wettability to an electrolysis solution in the end of carbon powder can be improved as a surface-active agent, For example, negative ion system surface-active agents, such as higher-fatty-acid ester and alkyl sulfate, Various surface-active agents, such as non-ion system surface-active agents, such as a high-class amine halogen acid salt and the 4th ammonium salt, a polyethylene glycol alkyl ether, and polyethylene glycol fatty acid ester, can be used. Especially, polyethylene-glycol stearate, polyoxyethylene nonyl phenol ether, higher-fatty-acid pentaerythritol, or its mono- fatty acid ester is mentioned as a suitable thing.

[0011]As for the surface-active agent amount of adsorption in the end of carbon powder, less than ten weight sections are preferred to 100 weight sections in the end of carbon powder, and its range of 0.5 to 6 weight section is more preferred. Since an addition of a conducting agent decreases relatively that the amount of adsorption is ten or more weight sections, the conductivity of positive electrode mixture falls and cell capacity falls, it is not desirable.

[0012]After the end of carbon powder is immersed in liquid in which low-boiling point solvents, such as water and alcohols, were made to distribute or dissolve a surface-active agent for example as a method of making a surface-active agent adsorbing in the end of carbon powder, a method of transpiring a solvent is mentioned, but. If it is the method that a surface-active agent may be made to adsorb effectively in the end of carbon powder, it can use without restriction especially. [0013]It kneads with binders, such as an active material and PTFE (polytetrafluoroethylene), and PVdF (polyvinylidene difluoride), and is used as positive electrode mixture the end of carbon powder a surface-active agent was made to adsorb.

[0014]Especially as an active material in this invention, although not restricted, for example as http://www4.ipdl.inpit.go.ip/cgi-bin/tran_web_cgi_cgic?atw_u=http%3A%2F%2Fwww4.ipdl.in..._7/30/2010 positive active material of a nonaqueous electrolyte battery, LiCoO₂, LiMn₂O₄, LiMnO₂, LiNiO₂, MnO₂, and CuO are illustrated. These active materials may use a kind independent and may use two or more sorts together if needed.

[0015]

[Function]Since the end of carbon powder the surface-active agent was made to adsorb as a conducting agent is used, the electrode for cells concerning this invention is good in the wettability to the electrolysis solution of an anode, and its effective surface area in an electrode reaction is large. For this reason, the electrode reaction in an anode comes to be uniformly performed on the surface of an active material, and the degradation speed of an active material becomes slow. [0016]

[Example]Although this invention is hereafter explained still in detail based on working example, in the range which is not limited at all by following working example and does not change the gist, it changes suitably and this invention can be carried out.

[0017](Working example 1) The cylindrical nonaqueous electrolytic solution secondary battery which uses the electrode for cells concerning this invention as an anode was produced. [Production of an anode] After mixing cobalt carbonate and lithium carbonate by the atomic ratio 1:1 of Co:Li, it heat-treated by 900 degreeC in the air for 20 hours, and LiCoO, was obtained. To

LICOO₂ as an active material obtained by carrying out such, PTFE as the surface treatment carbon powder end as a conducting agent and a binder was mixed by the ratio of the weight ratio 90:6:4, and positive electrode mixture was obtained to it. This positive electrode mixture was rolled in the foil of aluminum as a charge collector, it heat-treated under a 2-hour vacuum by 250 degreeC, and the anode was produced. As the above-mentioned end of surface treatment carbon powder, the thing to which one weight section of polyethylene-glycol stearate was made to stick to acetylene black 100 weight section was used.

[0018][Production of a negative electrode] To black lead of 400 mesh passes, it mixed by the ratio of the weight ratio 95:5, PTFE as a binder was rolled in the foil of aluminum as a charge collector, it heat-treated under a 2-hour vacuum by 250 degreeC, and the negative electrode was produced to it.

[0019][Preparation of a nonaqueous electolyte] In the mixed solvent of the volume mixture ratio 1:1 of ethylene carbonate and dimethyl carbonate, 1 mol/l. LiPF₆ was melted, and the nonaqueous electolyte was prepared to it.

[0020][Production of a cell] Cylindrical rechargeable battery BA1 (cell size: 14.2 mm in diameter, height:50.0mm) was produced using the above positive/negative two poles and nonaqueous electolyte. The microporous thin film made from polypropylene was used as a separator. [0021]Cell BA1 which drawing 1 is a sectional view of produced cell BA1, and is shown in the figure consists of the separator 3, the positive electrode lead 4, the negative electrode lead 5, the positive electrode outside terminal 6, the negative electrode can 7, etc. which isolate the anode 1 and the negative electrode 2, and these two electrodes. The anode 1 and the negative electrode 2

are accommodated in the negative electrode can 7 in the state where it was spirally rolled round via the separator 3 with which nonaqueous electrolyte was poured in, Via the positive electrode lead 4, to the positive electrode outside terminal 6, it can be connected to the negative electrode can 7 via the negative electrode lead 5, and the anode 1 can take out the negative electrode 2 now to the exterior again by making into electrical energy chemical energy produced in cell BA1 inside. [0022](Working example 2) Cell BA2 was produced like working example 1 except having used the thing to which one weight section of polyoxyethylene nonyl phenol ether was made to stick to acetylene black 100 weight section as the end of surface treatment carbon powder.

[0023](Working example 3) Cell BA3 was produced like working example 1 except having used the thing to which one weight section of higher-fatty-acid pentaerythritol was made to stick to acetylene black 100 weight section as the end of surface treatment carbon powder.

[0024](Comparative example 1) Comparison cell BC1 was produced like working example 1 except having used acetylene black of surface non-refining, without making a surface-active agent adsorb in production of positive electrode mixture.

[0025]Drawing 2 is the graph which took cell voltage (V) along the vertical axis, and took service capacity (mAh) along the horizontal axis and with which the initial discharge characteristic at 200 mA (constant current discharge) of cell BA1 using the electrode concerning this invention and comparison cell BC1 was expressed.

From the figure, cell BA1 using the electrode concerning this invention is compared with comparison cell BC1, and it is understood that service capacity is large.

Discharge made 2.75V discharge final voltage.

[0026]the cycle characteristic at 200 mA (constant current discharge) of cell BA1 using the electrode which <u>drawing 3</u> requires for this invention, and comparison cell BC1 — a vertical axis — the service capacity (mAh) of a cell — it is the graph which took the number of cycles (time) along the horizontal axis, and was expressed with it. It turns out that cell BA1 using the electrode concerning this invention is compared with comparison cell BC1, and the figure is excelled in the cycle characteristic. Charge and discharge made 2.75V discharge final voltage, and made 4.1V charge final voltage.

[0027]The rate of cycle degradation per 1 cycle after the cells BA1-BA3 using the electrode concerning this invention and the 500 cycle progress of comparison cell BC1 (%/cycle) is collectively shown in Table 1.

[Table 1]

	サイクル劣化率(%/サイクル)
電池BA1	0.034
電池BA2	0.043
電池BA3	0.044
比較電池BC1	0.046

[0029]Table 1 shows that compare the cells BA1-BA3 using the electrode concerning this invention with comparison cell BC1, and all excel [rate / of cycle degradation] in the cycle characteristic low. It turns out that especially cell BA1 especially using polyoxy-ethylene-glycol stearate as a surface-active agent reveals the outstanding cycle characteristic.

[0030](Working example 4) Produce six sorts of surface treatment acetylene black from which the amount of adsorption of polyoxy-ethylene-glycol stearate differs, and it is made to be the same as that of working example 1, Cell BA4 (the number of polyoxy-ethylene-glycol stearate adsorption parts: 0.1), Six sorts of cells 6 (tell BA5 (the number of the said adsorption parts: 0.5), cell BA6 (the number of the said adsorption parts: 2.0), cell BA7 (the number of the said adsorption parts: 5.0), cell BA8 (the number of the said adsorption parts: 10.0), and cell BA9 (the number of the said adsorption parts: 20.0) were produced.

[0031]drawing 4 — the service capacity (mAh) in early stages of each cell of the cells BA4-BA9 — a vertical axis — it is the graph with which the amount of adsorption (weight section) of the surface-active agent was expressed for the horizontal axis. Into the graph, the data of cell BA1 and comparison cell BC1 is also posted. It turns out that it is preferred that they are less than ten weight sections to acetylene black 100 weight section in order to enlarge early service capacity as for the amount of adsorption of a surface-active agent, and the range of 0.5 to 6 weight section is more preferred than the figure. The same result is obtained when other end of carbon powder and a surface-active agent are used.

[0032]Although above-stated working example explained the example in the case of applying this invention to the anode of a nonaqueous electrolytic solution secondary battery, the drainage system of an electrolysis solution, a non-drainage system and primary [of a cell], and in particular secondary are not restricted.

[0033]

[Effect of the Invention] Since the wettability to the electrolysis solution of an active material is improved when the electrode concerning this invention makes a surface-active agent adsorb in the end of conducting agent slack carbon powder, the characteristic effect production of the cell which reveals the outstanding battery characteristic excelled [effect] in this invention, such as becoming possible, is done so.

[Translation done.]